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Substituted polynorbornenes as promising materials for gas separation membranes †

E Sh Finkelshtein, M V Bermeshev, M L Gringolts, L E Starannikova, Yu P Yampolskii

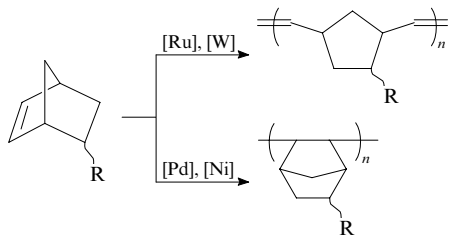
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Abstract. Published results concerning the synthesis and study of the transport characteristics of polynorbornenes are considered and analyzed. Conclusions are drawn regarding the effect of the backbone rigidity and the nature of side groups on the gas permeability level. The prospects of using addition organosilicon polynorbornenes as gas separating membrane materials are discussed. The bibliography includes 88 references.

I. Introduction

Polymerization of norbornenes is an efficient tool for macromolecular design because it employs readily accessible monomers and the process can follow different mechanisms to give polymers with different backbone structures.[1, 2]



E Sh Finkelshtein, M V Bermeshev, M L Gringolts, L E Starannikova, Yu P Yampolskii A V Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prosp. 29, 119991 Moscow, Russian Federation. Fax: (7-495) 633 85 20,
tel. (7-495) 955 43 79, e-mail: fin@ips.ac.ru (E Sh Finkelshtein),
tel. (7-495) 955 43 01, e-mail: bmv@ips.ac.ru (M V Bermeshev),
tel. (7-495) 955 42 80, e-mail: gringol@ips.ac.ru (M L Gringolts),
tel. (7-495) 955 42 12, e-mail: Luda@ips.ac.ru (L E Starannikova),
tel. (7-495) 955 42 10, e-mail: yampol@ips.ac.ru (Yu P Yampolskii)

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The polymerization route depends on the catalytic system chosen. The 'framing' of the backbones is controlled by the structure and the number of substituents in the initial monomers. The structural diversity of polynorbornenes makes them suitable for various purposes, in particular, as promising membrane materials, which provide unique possibility for studying the fundamental correlations 'structure – gas separation properties'. The found correlations can be used for deliberate design of polymeric membranes with a set of definite characteristics needed to solve particular tasks.

The gas separating properties of the polymeric materials are based on their ability to perform selective mass transfer. A physical characteristics of this process is the permeability coefficient (P). In non-porous polymeric films (membranes), the mass transfer occurs by the solution – diffusion mechanism. The essence of this mechanism is that the concentrations of the penetrant on the boundary surfaces of the membrane are different, being determined by the partial pressures in the gas phase before and after the membrane. This concentration gradient gives rise to a gas flow (J) through the membrane.[3]

The permeability coefficient is determined by the equation

$$J = P\,\frac{\Delta p}{l},$$

where Δp is the pressure drop on the membrane, l is the membrane (film) thickness.

In view of the above information about the solution – diffusion mechanism in non-porous polymeric membranes, the permeability coefficient can be represented as the product

$$P = D \cdot S,$$

† Dedicated to Academician S N Khadzhiev on the occasion of his 70th birthday.

where D is the diffusion coefficient, S is the solubility coefficient.

The diffusion coefficient is the kinetic factor of permeability, *i.e.*, it characterizes the mobility of gas molecules and depends on their sizes, while the solubility coefficient is the thermodynamic factor determining the gas affinity to the polymer matrix and characterizing the driving force of the process. The unit of measurement of the permeability coefficient is called Barrer:

$$1\ \text{Barrer} = 10^{-10}\ \text{cm}^3\,(\text{STP})\ \text{cm}\ \text{cm}^{-2}\ \text{s}^{-1}\,(\text{cm Hg})^{-1}$$

Yet another key parameter of a membrane is the selectivity of gas separation (α_{AB}) defined as

$$\alpha_{AB} = \frac{P_A}{P_B},$$

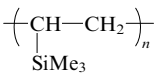
where P_A and P_B are the permeability coefficients of gases A and B. For most pairs of gases (A and B) and polymeric membranes, the permeability and selectivity are inversely related: higher permeability is accompanied by lower selectivity and *vice versa*.[4]

As a rule, glassy polymers are more effective for the separation of light gases such as H_2, He, O_2, N_2 and CO_2 where the separation parameters are mainly determined by the kinetic permeability factor: smaller gas molecules penetrate faster through the membrane.

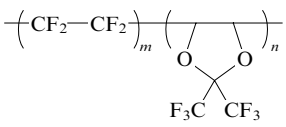
In highly elastic polymers, 'thermodynamic' selectivity predominates; hence, they are better suited for the separation of C_1-C_5 hydrocarbons. The selectivity is mainly determined by the solubility coefficients: being more readily soluble, heavier gases penetrate faster through the membrane.

However, there are important exceptions: some glassy polymers (in particular, polyacetylenes) exhibit membrane properties that are more typical of elastomers, *i.e.*, the gas transport in them is controlled by the solubility in the polymer matrix.

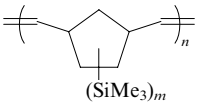
Among the glassy polymers that show diffusional (sometimes called 'sieve') selectivity, note, for example, poly(vinyltrimethylsilane),[5] polynorbornenes obtained by metathesis polymerization (MP) (below referred to as metathesis polynorbornenes) (see Section II), organofluorine polymers.[6,7]



Poly(vinyltrimethylsilane)



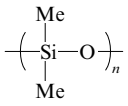
Organofluorine polymers



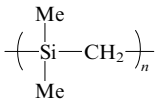
$m = 1, 2.$

Metathesis polynorbornenes

Polysiloxanes[8] and polysilmethylenes[9] are typical and fairly effective elastomer membrane materials

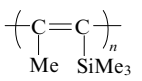


Poly(dimethylsiloxane)

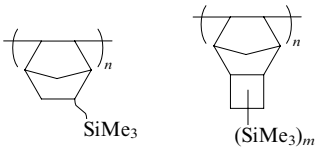


Poly(dimethylsilmethylene)

Glassy polymers that show the 'thermodynamic' selectivity include the above-noted polyacetylenes[10–12] and silicon-substituted polynorbornenes obtained by addition polymerization (AP) (addition polynorbornenes) (see Section IV).



Poly(trimethylsilylpropyne)



$m = 1, 2.$

Addition polynorbornenes

Currently, membrane methods find increasing application for the isolation, separation and concentration of gases, thus competing with traditional methods, in particular, with cryogenic distillation and adsorption or absorption of gases.[13] This is caused by a number of advantages of the membrane gas separation: low net cost of the equipment, short pay-off period, small dimensions, low power consumption, environmental cleanness and higher safety. Today gas separation by means of polymer membranes is a widely used industrial method for the production and purification of gases, in particular, production of nitrogen from air (with a purity of up to 99% or even higher), hydrogen recovery and concentration from process streams of chemical, petrochemical and petroleum refining industries; removal of CO_2 from natural gas, and decrease in the atmospheric discharge of CO_2.[14–16]

In industrial membrane modules, industrially produced polymers such as polysulfones, polyimides, polycarbonates, cellulose acetate, *etc.* mainly serve as membrane materials.[3] They have high selectivity for non-condensed gases (H_2, He, O_2, N_2) and good mechanical properties. Nevertheless, each polymer has its own drawbacks; therefore, new highly permeable and highly selective polymeric membrane materials meant for solving particular tasks need to be developed.

These tasks served as natural and obvious impetus for synthetic chemists to develop effective methods for targeted synthesis of specified macromolecular structures with potentially high gas separation characteristics.

Ideally, a membrane should be highly permeable and highly selective, have good mechanical and film-forming properties and be stable (physically and chemically) in contact with the separated media. However, as noted above, the permeability and the selectivity are usually inversely related, at least, for light gases. This behaviour is attributable to the properties of proper polymers and is not related to the polymer interaction with gases. Therefore, for each particular process, it is necessary to select the macromolecular structure with the optimal permeability to selectivity ratio.

Thus, relying on the existing experimental data on the relationship between the structure and transport properties of polymers, a synthetic chemist should outline the poly-

meric structure that would, most likely, possess the desired gas separation properties and then develop acceptable methods for the synthesis of the corresponding monomers (as a rule, unknown previously) and for their polymerization and also practically implement everything listed above. The polymers thus obtained should possess good film-forming properties (*i.e.*, have high molecular masses). A failure at any of the above stages would considerable reduce the value of the whole previous work, if not obliterate it completely.

This review is devoted to the methods of synthesis and gas separation characteristics of polynorbornenes, which represent a relatively new class of promising membrane materials. Some of them are among the most permeable polymers (see Section V).

Note that this review does not claim to cover the whole huge material on the polymerization of norbornene. This has already been the subject of a number of reviews and chapters of monographs (see, for example, Refs 1, 17–19). However, in our opinion, polynorbornenes have occupied the deserved position in the science of membranes, and now it is pertinent to analyze literature data that reflect the efforts of many researchers aimed at the development of highly permeable membrane materials based on these polymers. Most of the publications cited in this review were published from 1995 to 2010.

II. Metathesis polymerization of norbornenes as a method for the synthesis of membrane materials

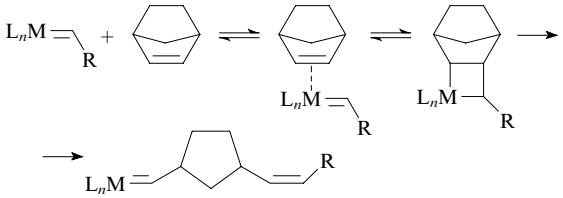
The metathesis polymerization of cycloolefins is a kind of metathesis reaction. It is accompanied by ring opening and is referred to as Ring Opening Metathesis Polymerization (ROMP).[1] As the conventional metathesis reaction, ROMP is in principle reversible. However, during the ROMP of strained cyclic molecules such as norbornene, the ring strain relief upon ring opening becomes the thermodynamic driving force, resulting in the irreversible formation of the corresponding polymers. The norbornene strain energy is 100 kJ mol^{-1} and the Gibbs energy ($-\Delta G^{\circ}$) of the ROMP of norbornene is 47 kJ mol^{-1}. Therefore, norbornene is a monomer of choice for this type of polymerization.

Currently, it is generally accepted that metathesis of olefins and cycloolefins follows a chain carbene mechanism.[20–22] In the case of norbornene, at the initiation step, the starting metal carbene [$L_nM(=CHR)$, M is transition metal] is converted to secondary metal carbene *via* coordination to cycloolefin, [2 + 2] cycloaddition and decomposition of the metallacyclobutane intermediate, and the resulting carbene performs polymerization at the chain propagation step (Scheme 1). Chain termination is induced by the addition of a special reagent able to form inactive metal carbene.[23]

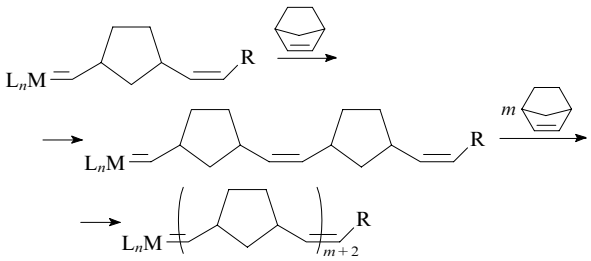
Catalytic systems for ROMP can be classified into two large groups: (i) systems that form metal carbenes *in situ* during the reaction under the action of an activator (promoter) (so-called 'classical' metathesis catalysts) and (ii) one-component systems representing pre-formed metal alkylidene complexes M(=CRR′) (where R and R′ are alkyl, aryl or other hydrocarbyl groups).[1,17] The former group of catalysts is usually represented by transition metal salts and oxides (W, Re, Ru, Mo, *etc.*) activated, for example, by organoelement compounds or terminal alkynes.

Scheme 1

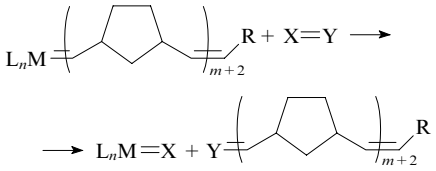
Initiation



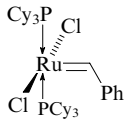
Chain propagation



Chain termination



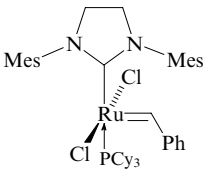
They are readily accessible, fairly effective and are used in a number of large-scale industrial processes.[1,24] The main advantages of the latter group of catalysts include stability, high activity, high tolerance to functional groups and the ability to perform 'living' polymerization of cycloolefins, in particular, norbornene. They have been called well-defined catalysts. For example, the Grubbs and Schrock complexes **1**–**4** belong to this group [17,25,26]



1

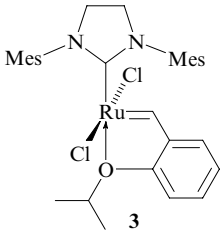
Grubbs catalyst of the first generation (Grubbs I)

Cy is cyclohexyl.



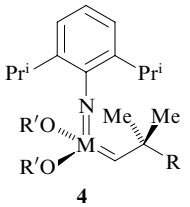
2

Grubbs catalyst of the second second generation (Grubbs II)



3

Grubbs–Hoveyda catalyst



4

M = Mo, W; R = Me, Ph; R′ = Alk, Ar.

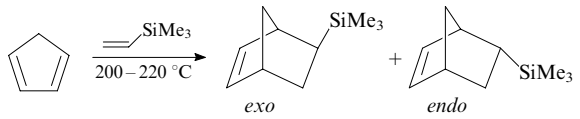
Schrock catalysts

The works on the synthesis of metathesis polynorbornenes in view of their gas separation properties were started at the turn of the 1980s and the 1990s in Japan and

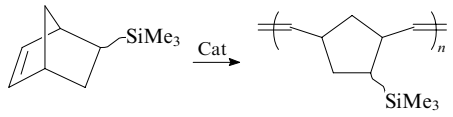
Russia.[27–29] The first publications were devoted to their organosilicon derivatives; later, these objects were found to be very interesting for the systematic research of gas permeability.

1. Silicon-substituted metathesis polynorbornenes

Experimental data indicating the considerable influence of silicon-containing substituent on the gas permeability of metathesis polynorbornene were obtained in the synthesis and study of poly(5-trimethylsilylnorbornene).[28,29] The initial monomer was synthesized by high-temperature Diels–Alder condensation of cyclopentadiene (CPD) and trimethylvinylsilane where the target product contained almost equal amounts of the *exo*- and *endo*-isomers.

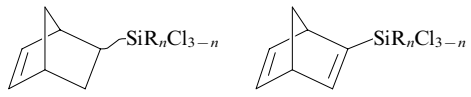


This is a rather important fact, because the Diels–Alder reactions normally tend to give mainly *endo*-isomers,[30,31] which are less reactive in the polymerization transformations.[1,18,19] The polymerization of 5-trimethylsilylnorbornene was performed on W, Ru and Re catalysts and resulted in high yields of polymers (Table 1).



A broad range of silicon-substituted polynorbornenes have now been synthesized in order to elucidate the dependence of their gas separation characteristics on the structure of the monomer unit.

The key method used for the synthesis of silicon-substituted norbornene and norbornadiene monomers



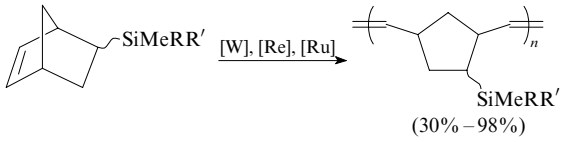
$n = 1-3$.

is the Diels–Alder condensation of CPD (or dicyclopentadiene) with silicon-substituted ethylenes or acetylenes ($H_2C{=}CHSiR_nCl_{3-n}$, $HC{\equiv}CSiR_nCl_{3-n}$, $n = 1-3$), which forms the norbornene fragment. Electron-withdrawing substituents containing Si–Cl bonds accelerate the reaction.[31,41]

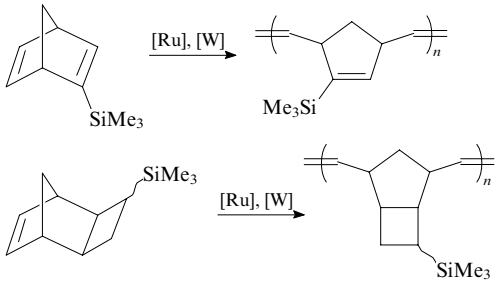
Other approaches to the synthesis of silylnorbornenes and -norbornadienes use a pre-formed bicyclic molecule. Examples are provided by hydrosilylation of norbornadiene with chloro- or alkylsilanes in the presence of molybdenum catalysts,[42] metallation of norbornadienes with lithium or sodium followed by the reaction with chloroalkylsilanes,[43] the reaction of (norbornenylmethyl)magnesium halides with organochlorosilanes.[32]

Silicon-substituted tricyclo[4.2.1.$0^{2,5}$]non-7-enes (below referred to as tricyclononenes) synthesized by [2+2+2] cycloaddition of chlorosilylethylenes to quadricyclane[34,44] were also used as monomers (for more details, see Section IV).

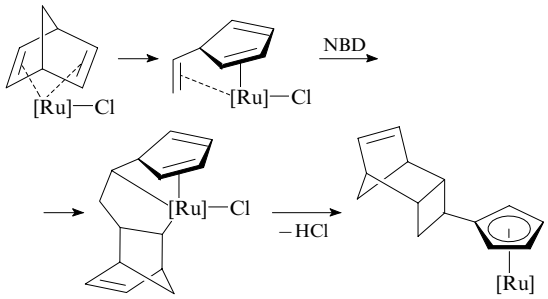
The metathesis polymerization of silicon-substituted norbornenes and their analogues, substituted norbornadienes and tricyclononenes, was performed using tungsten and rhenium catalytic systems and also aqueous ruthenium trichloride and generation I and II Grubbs catalysts (see Table 1). Phenylacetylene, 1,1,3,3-tetramethyldisila-1,3-cyclobutane (TMSB), Bu^i_2AlCl and some other organoelement compounds served as activators of WCl_6. Activation of Re_2O_7/Al_2O_3 was done by tetraethyllead or tetrabutyltin; for $RuCl_3 \cdot x\,H_2O$, alcohols were used. The Grubbs catalysts did not require activation.



R′ = Me: R = Me, CH_2SiMe_3, Ph; R = R′ = Pr^i.

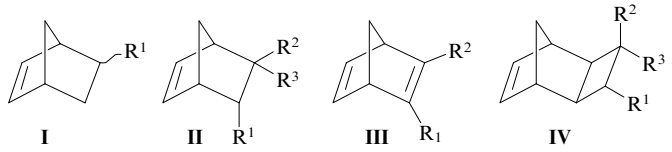


The WCl_6–TMSB system and the Grubbs carbene complexes were the most active catalysts of the ROMP of the studied silicon-substituted norbornenes. As can be seen from Table 1, they provide the yields of polymers of up to 98% with molecular masses of $\sim 10^6$. Lower activities were found for the aluminium–rhenium catalyst and the $RuCl_3$–ROH system. The latter was inactive in the polymerization of norbornadiene and its silicon-substituted derivatives.[34,38] A probable reason for this behaviour is the higher ability of norbornadienes to be coordinated to the catalyst.[1] Deactivation of the active site by the mechanism reported[45] for unsubstituted norbornadiene (NBD) is also possible.



Norbornenes and norbornadienes with the $SiMe_3$, $(CH_2)_nSiMe_3$ ($n = 1-3$), $SiMePr^i_2$ and $SiMe_2Ph$ substituents are fairly active in the ROMP and form high-molecular-mass polymers[29,36,38] in high yields at the ratio monomer : catalyst = 700–3000 (see Table 1). A somewhat different behaviour was demonstrated by norbornenes with substituents containing Si–O–Si bonds. A recent publication[35] deals with the behaviours of different 5-oligosiloxanyl norbornenes in the ROMP induced by the Grubbs catalysts of different generations. The monomer, *viz.*, nor-

Table 1. Metathesis polymerization of silicon-substituted norbornenes, norbornadienes and tricyclononenes.

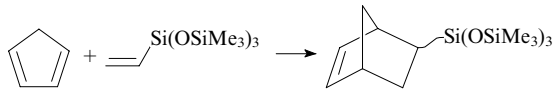


I **II** **III** **IV**

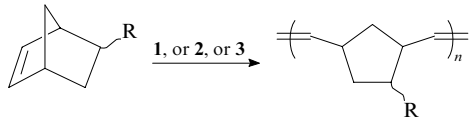
R^1	R^2	R^3	Catalyst [a]	The ratio [M] : [Cat] [b]	Polymer yield (%)	$M_w \times 10^{-3}$	M_w/M_n	Content of *cis*-units (%)	Ref.
Monosubstituted norbornenes (**I**)									
$SiMe_3$			A	1000	99	4.0 [c]	–	–	32
			B	180	78	620	1.8	7	33
			C	3000	98	500	2.2	28	34
$SiMe_2CH_2SiMe_3$			D	750	81	2.0 [c]	–	–	29
			E	350	30	1.7 [c]	–	–	29
$SiMe(OSiMe_3)_2$			C	200	96	309	2.7	–	35
			F	150	95	619	5.0	–	35
$Si(OSiMe_3)_3$			C	100	95	600	2.5	–	35
$SiMe_2Ph$			A	500	96	617	3.3	30	36
			B	180	79	247	2.2	2	36
			C	3000	98	490	2.5	46	36
$SiMePr^i_2$			A	500	98	895	1.8	38	36
			B	180	82	180	1.7	3	36
			C	3000	95	670	1.5	40	36
CH_2GeMe_3			B	47	73	234	2.0	5	37
Disubstituted norbornenes (**II**)									
H	CN	$SiMe_3$	G	150	24	191	3.0	–	27
H	CN	CH_2SiMe_3	H	177	17	105	2.4	–	27
H	CN	$SiMe_2SiMe_3$	H	52	6.1	348	5.2	–	27
H	CN	$SiMe_2OSiMe_3$	H	52	38	576	2.9	–	27
H	CN	$CH_2SiMe_2OSiMe_3$	H	54	11	–	–	–	27
$SiMe_3$	$SiMe_3$	H	A	50	93	290	3.1	54	38
			B	80	73	633	1.7	6	38
H	$SiMe_3$	$SiMe_3$	A	100	98	1500	3.2	60	39
			B	80	50	100	1.8	1–2	39
Norbornadienes (**III**)									
$SiMe_3$	H		I	50	46	26	3.3	–	40
			A	70	97	51	2.9	42	38
$SiMe_2(CH_2)_3SiMe_3$	H		A	250	70	549	3.1	43	38
$SiMe_3$	$SiMe_3$		A	100	98	1600	2.8	71	34
			C	1000	98	220	1.2	11	34
Tricyclononenes (**IV**)									
$SiMe_3$	H	H	A	500	98	1200	2.2	–	36
			C	3000	98	634	1.5	10	36
$SiMe_3$	$SiMe_3$	H	A	100	98	1000	1.6	47	34
			C	1500	97	800	1.8	22	34
H	$SiMe_3$	$SiMe_3$	A	100	98	640	2.0	–	36
			C	1500	97	347	1.6	28	36

[a] Catalysts and temperature of the process: A, WCl_6-TMSB, 20 °C; B, $RuCl_3 \cdot x\,H_2O-EtOH$, 60–75 °C; C is the Grubbs I catalyst (**1**), 20 °C; D, $WCl_6-PhC{\equiv}CH$, 20 °C; E, $Re_2O_7-Al_2O_3-SnBu^n_4$; F, is the Grubbs II catalyst (**2**), 20 °C; G, WCl_6-Et_3Al; H, $WCl_6-Bu^i_3Al-CH_2{=}CHC_6H_{13}$-n, 80 °C; I, $WCl_6-SnBu^n_4$; [b] M is monomer; [c] intrinsic viscosity in dl g^{-1}.

bornene with one substituent containing three Me_3SiO groups, was synthesized by the Diels–Alder reaction.



Among the three Ru carbene catalysts **1**–**3**, the Grubbs I catalyst (**1**) proved to be most efficient (see Table 1). In other cases, the formation of insoluble polymers or very broad molecular-mass distributions (MMD) was observed.

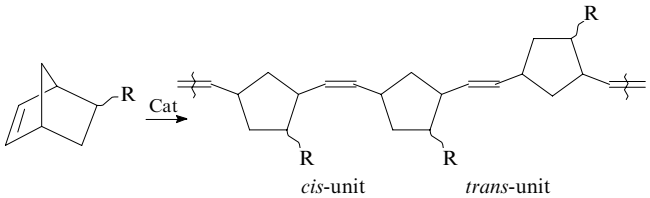


R = $SiMe(OSiMe_3)_2$, $Si(OSiMe_3)_3$,
$SiMe_2(OSiMe_2)_nOSiMe_3$ (n = 1, 3, 8).

The authors attributed this fact to the high activity of the Grubbs II and the Grubbs–Hoveyda catalysts, which leads to the formation of high-molecular-mass and, hence, insoluble polymers. The same reason accounts for the increased contribution of intra- and inter-molecular chain transfer reactions, resulting in high polydispersity of the polymers (M_w/M_n of up to 7.3). The lack of clear correlation between M_n of the polymer and the monomer : catalyst ratio together with broad MMD attest to the absence of living polymerization.

It is noteworthy that for the above-mentioned monomers, binary catalytic systems (WCl_6-Ph_4Sn and $MoCl_5-Ph_4Sn$) were inactive. Polymerization of norbornenes with bulky siloxane groups giving rise to soluble high-molecular-mass polymers with satisfactory film-forming properties was accomplished using the Grubbs I catalyst at relatively low (100–200) monomer : catalyst molar ratios.

A specific feature of metathesis polynorbornenes is stereoisomerism related to the *cis*- or *trans*-configuration of the double bonds formed.

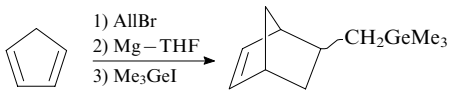


R = H, $SiMe_3$.

In the synthesized silicon-substituted polymers, the *cis* : *trans* ratio of the double bonds can usually be determined by NMR spectroscopy, based on the ^1H NMR signals of the allyllic hydrogen atoms and/or ^{13}C NMR signals of the allyllic carbon atoms.[38,40,46–48] It can be seen from Table 1 that ROMP catalysts have different types of stereoselectivity. The highest *trans*-selectivity is found for the $RuCl_3-EtOH$ catalyst, which initiates the formation of a polymer containing up to 97% of *trans*-double bonds. The W systems are least selective; they provide polymers with nearly equal contents of *cis*- and *trans*-double bonds. The Grubbs catalyst is sensitive to the monomer structure and generally promotes the *trans*-configuration. Polynorbornenes with predominant contents of *cis*-double bonds can be obtained using Re catalytic systems.[1,46]

In order to study the effect of polynorbornene microstructure on the gas separation properties, the metathesis homopolymers of norbornene and 5-trimethylsilylnorbornene with different contents of *cis*- and *trans*-units were obtained in the presence of Ir, Re, Ru and W catalysts.[46–48]

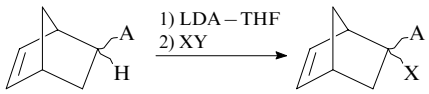
For investigating the gas separation properties, the trimethylgermyl polynorbornene derivative was prepared.[37] The monomer was synthesized from halomethylnorbornene formed as the adduct in the Diels–Alder condensation of CPD and allyl halide.



(68%)

The polymerization was catalyzed by the $RuCl_3-EtOH$ and $RuCl_2(PPh_3)_3$ catalytic systems (see Table 1).[37]

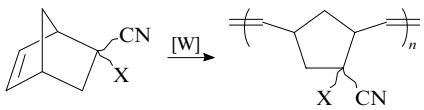
Metathesis polynorbornenes with two substituents in the monomer unit were also prepared. A series of CN- and CO_2Me-containing disubstituted metathesis polynorbornenes have been described;[27] their gas separation characteristics were determined. As the second substituent, various alkyl groups (Me, Et, Pr^n, Bu^n) and oligosilanyl and oligosiloxanyl groups were tested. The key issue in the synthesis of monomers was proton elimination from the C(5) atom of 5-cyanonorbornene induced by lithium diisopropylamide (LDA). At the second step, the desired electrophilic agent was added to the anion thus produced, giving rise to the target monomer.



(40%–87%)

A = CN, CO_2Me; X = Alk, oligosiloxanyl, oligosilanyl;
Y = Cl, Br.

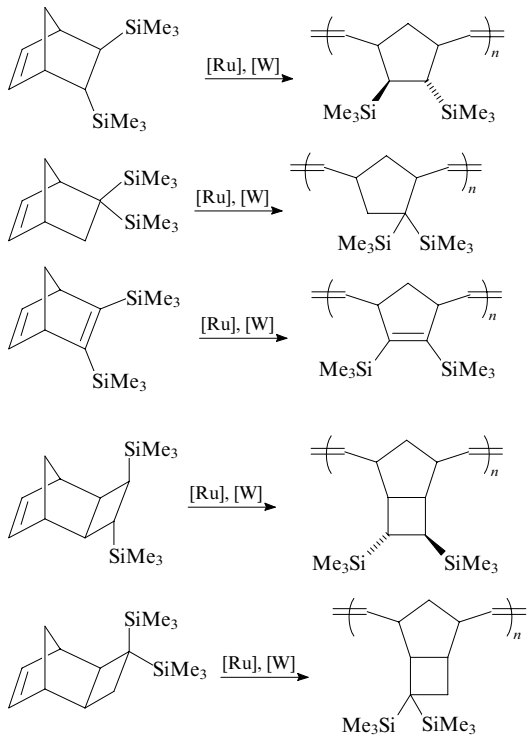
The metathesis polymerization of the synthesized monomers was successfully performed on a W-based catalytic system ($WCl_6-AlBu^i_3$–oct-1-ene) at 80 °C (see Table 1) and at relatively low monomer : WCl_6 ratios (50–177); the molecular mass of the obtained polymers reached 5×10^5, the MMD value varied from 1.6 to 5.2.



As shown below, CN derivatives of polynorbornene are low-permeable polymers irrespective of the silicon-containing substituent in the geminal position.

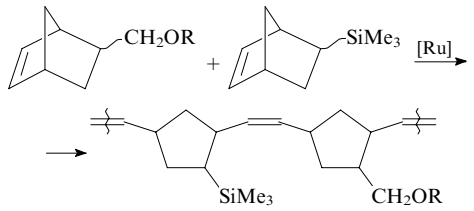
A sharp increase in the gas permeability follows from the introduction into the monomer unit of two $SiMe_3$ groups bonded directly to the five-membered ring. Recent publications[34,38] present a detailed study of the ROMP of norbornenes, norbornadiene and tricyclononenes with two $SiMe_3$ substituents using various catalytic systems: the

Grubbs I complex, WCl_6-TMSB and $RuCl_3 \cdot x H_2O-EtOH$ (see Table 1). The synthesis of monomer is described in Section IV.



The trends found for the ROMP of monosilicon-substituted norbornenes were also retained for disilicon-substituted norbornenes and norbornadienes. In particular, 2,3-bis(trimethylsilyl)norbornadiene was not polymerized on the $RuCl_3 \cdot x H_2O-EtOH$ catalyst.[34]

Other objects for investigating the gas separation properties are copolymers of norbornene and its derivatives. The synthesis of random copolymers of 5-trimethylsilylnorbornene with 5-trimethylsiloxymethylnorbornene and 5-hydroxymethylnorbornene was reported.[34]



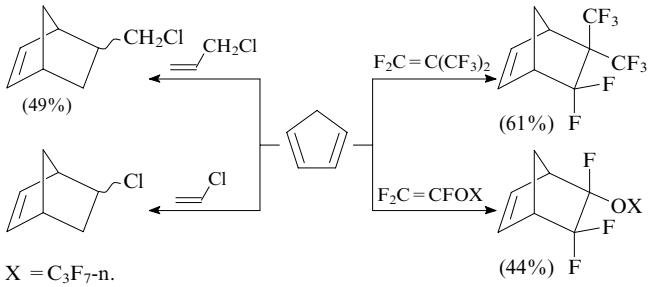
R = H, Me_3Si.

The reaction was catalyzed by systems based on $RuCl_3$ and $RuCl_2(PPh_3)_3$ and by the Grubbs I complex. The yields of copolymers were much higher (up to 98%) with the last-mentioned catalyst at relatively high monomer : catalyst ratios (up to 1000). Note that 5-hydroxymethylnorbornene is a less reactive comonomer, as the hydroxy group can react with the catalyst.[17]

2. Halogen-containing metathesis polynorbornenes

A series of chloro- and fluoro-containing polynorbornenes have been prepared.[49, 50] The corresponding monomers were synthesized by the Diels–Alder reaction (Scheme 2).

Scheme 2



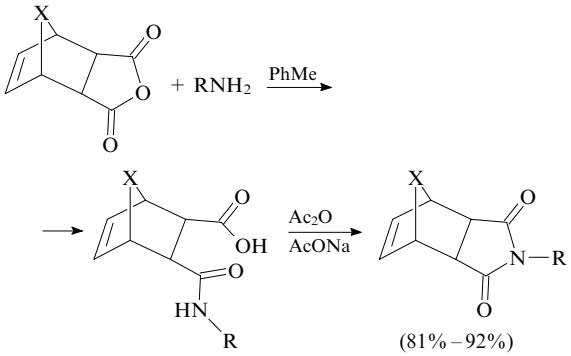
X = C_3F_7-n.

The WCl_6-TMSB and $WCl_6-(Me_3SiCH_2)_4Sn$ systems were used in the synthesis of fluorine-containing polynorbornenes. The molecular masses (M_w) of the polymers varied from 5×10^4 to 1×10^5, the yields were 55%–63%.

Chlorinated norbornenes were polymerized using catalytic systems based on WCl_6, Re_2O_7 and $RuCl_3-EtOH$. The yields of polymers were 40%–100%.

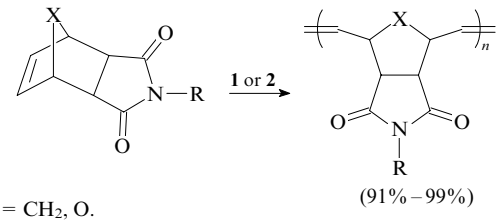
3. Polymeric norbornenedicarboximides

A group of Mexican researchers synthesized an extensive series of substituted norbornenedicarboximides. The starting anhydride was obtained from dicyclopentadiene and maleic anhydride by the Diels–Alder reaction.



X = CH_2, O; R = cyclo-C_5H_9, cyclo-C_6H_{11}, Ph, 4-$CF_3C_6H_4$, 3,5-$(CF_3)_2C_6H_3$, C_6F_5, Ad (Ad is 1-adamanthyl).

The synthesized monomers were mixtures of *exo*- (~90%) and *endo*- (~10%) isomers. These were converted to the corresponding polynorbornenes, and the gas separation characteristics of the polymers were studied.[51–58]



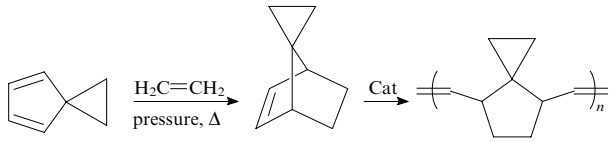
X = CH_2, O.

Polymerization of norbornenedicarboximides was performed most often in the presence of the Grubbs II ruthenium carbene complexes. The polymers were prepared in high yields and with high molecular masses ($M_n \approx 10^5$) at relatively narrow MMD (1.1–1.3). The polymers showed a dependence of the glass transition temperature (155–220 °C) on the nature of the N-substituent. The thermal stability of this group of polymers is very high (up to 400 °C). The density of all of the synthesized poly(nor-

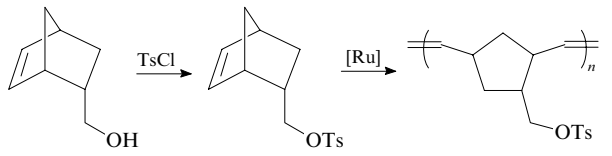
bornenedicarboximides) was higher than 1 g cm^{-3}. The introduction of fluorine-containing groups as substituents at nitrogen resulted in further increase in the density. Measurements of the mechanical strength of these polymers showed rather high values: rupture strength of 40 to 67 MPa, the Young modulus of up to 1.5 GPa. Examples of synthesis of various copolymers of N-substituted norbornenedicarboximides on the Grubbs catalysts were reported.[52, 54, 58]

4. Other metathesis polynorbornenes

In order to study the gas separation properties, the ROMP of spirocyclopropane-1,1′-norbornene was carried out in the presence of catalytic systems based on WCl_6, $RuCl_3$ and Re_2O_7. The yields of polymers varied over a broad range, the content of *cis*-units varied from 4 ($RuCl_3$) to 75% (WCl_6).[32, 49, 59, 60] Note that norbornenes with 7-substituents are less reactive than unsubstituted norbornene, as the substituent shields the double bond, thus hampering its coordination to the catalyst.

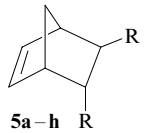


A new monomer and polymer were synthesized[61] with the goal of designing a polymeric material for the separation of nitrogen – oxygen mixtures.



Polymerization was carried out in the presence of either ruthenium carbene complexes or a binary system based on $Ru(PPh_3)_3Cl_2$ (phenylacetylene or trimethylsilylacetylene was used as the activator). The polymer yields reached 89% at relatively broad MMD (up to 3.7). According to the data from NMR spectroscopy, the polymer units were mainly *trans*-configured.

A series of norbornene derivatives **5a** – **h** containing two substituents with either ester or keto groups were synthesized and introduced in the ROMP in order to obtain permeable polymeric matrices for oxygen sensors.[62]



5a – **h**

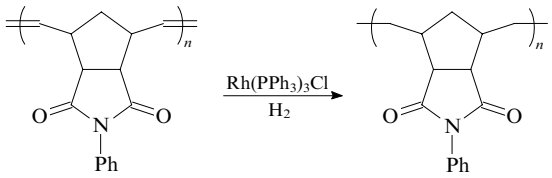
R = CH_2OBz (**a**), Bz (**b**), C(O)OR′ [R′ = Bn (**c**), $CH_2C_6H_4Bu^t$-4 (**d**), $(CH_2)_3OC_6H_3Bu^t_2$-2,4 (**e**), Me (**f**), Bu^t (**g**), CH_2Bu^t (**h**)].

The ROMP was catalyzed by the modified Grubbs catalyst of generation II. This gave polymers with M_n = 42 500 – 165 300 at the monomer : catalyst molar ratio of 200 or 300. The catalyst provided rather narrow MMD (1.04 – 1.2).

5. Hydrogenated metathesis polynorbornenes

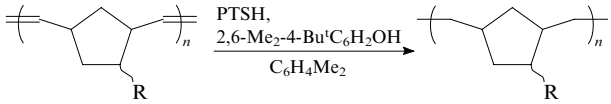
The presence of double bonds in metathesis polynorbornenes makes them chemically and thermally unstable. Therefore, works aimed at their hydrogenation were undertaken. Currently, quite a few examples of the reduction of metathesis polymers both in the presence of polymerization catalysts (tandem processes) and under the action of special catalysts have been reported.[1, 17, 63, 64]

For example, Wilkinson's catalyst was used for hydrogenation of metathesis polynorbornene.[56]



(99%)

Metathesis polynorbornenes were also reduced with *p*-toluenesulfonylhydrazide (PTSH).[1, 35] Comparison of the molecular masses of the reduced polymer with the unsaturated precursors shows the absence of backbone cleavage during hydrogenation.[35]



R = $SiMe(OSiMe_3)_2$, $Si(OSiMe_3)_3$.

The absence of ^{1}H NMR signals in the olefin region served as evidence for stating that the reduction of metathesis polynorbornenes was quantitative.[35]

Analysis of the literature shows that ROMP makes it possible to construct polynorbornene structures with almost any number and type of regularly varied side groups and with different stereo structure of the backbone over a broad range of molecular masses. Usually, metathesis polymers have good film-forming properties, which is rather important for the measurement and investigation of the gas separation characteristics.

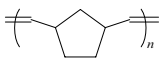
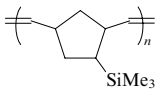
III. Gas separation properties of metathesis polynorbornenes

1. Silicon-substituted polynorbornenes

Silicon-substituted polynorbornenes show the highest permeability coefficients among metathesis polymers.

The gas separation characteristics of unsubstituted polynorbornene and poly(5-trimethylsilylnorbornene) synthesized using various catalytic systems are presented in Table 2. It can be seen that the introduction of $SiMe_3$ groups is accompanied by approximately an order of magnitude increase in the gas permeability coefficients. The glass transition temperature (T_g) of the polymer also considerably increases (from 42 to 106 °C), which attests indirectly to increase in the polymer chain rigidity, which probably increases the permeability. The packing of more rigid chains is less dense, and, as a consequence, the free volume increases as compared with that of unsubstituted polynorbornene. In many cases, there is actually a correlation between T_g and the gas permeability of polynorbornenes, especially for structurally similar macromolecules.

Table 2. Effect of the type of catalyst of the metathesis polymerization of norbornene and 5-trimethylsilylnorbornene on the gas separation characteristics of the resulting polymers.

Polymer	Catalyst	T_g /°C	The *cis* : *trans* ratio	*P* /Barrer						α_{AB}		Ref.
				H_2	He	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4	
	$RuCl_3 \cdot x H_2O - EtOH$	35	20 : 80	7.3	6.0	–	0.2	3.1	0.26	–	11.9	48
	$WCl_6 - PhC{\equiv}CH$	42	55 : 45	19.4	13.0	2.6	0.75	13.9	1.9	3.5	7.3	48
	$Re_2O_7 - Al_2O_3 - PbEt_4$	43	70 : 30	17.7	12.9	3.2	0.8	14.4	1.4	4.0	10.3	48
	$WCl_6 -$ TMSB	31	60 : 40	21	–	2.8	1.5	15.4	2.5	1.9	6.3	46
	$ReCl_5 - EtAlCl_2 - CH_2{=}CHCO_2Et$	67	> 98 : 2	–	23.0	7.5	2.2	23.6	4.7	3.4	5.0	46
	$IrCl_3 \cdot x H_2O/EtAlCl_2$	36	12 : 88	–	24.0	3.2	0.7	14.5	2.2	4.6	6.6	46
	Grubbs I (**1**)	107	28 : 72	65	50.0	16.9	4.2	63.4	7.3	4.0	8.7	34
	$RuCl_3 \cdot x H_2O - EtOH$	85	5 : 95	66.8	51.2	16.5	4.8	65.7	4.8	3.4	13.7	47
	$WCl_6 - PhC{\equiv}CH$	106	57 : 43	76.8	58.4	20.9	6.2	79.3	17.0	3.4	4.7	47
	$Re_2O_7 - Al_2O_3 - PbEt_4$	59	75 : 25	–	56.0	18.0	4.4	72.0	9.2	4.1	7.8	47

However, there are examples where there is no such correlation; these are considered below.

As noted in the previous Section, the use of different catalysts gives rise to metathesis polynorbornenes that differ in the microstructure, in particular, in the contents of *cis*- and *trans*-double bonds. It follows from Table 2 that the transport properties of metathesis poly(5-trimethylsilylnorbornenes) synthesized using different catalysts and having different *cis* to *trans* ratios do not differ much. The polymers with higher contents of *cis*-bonds have somewhat higher permeability coefficients. A similar trend is also observed for unsubstituted polynorbornene (see Table 2). Little is known about the influence of the *cis* : *trans* ratio at the double bonds on the gas permeability.[12, 47, 65] This may be related to the difficulty of preparing a set of polymer structures with a specified *cis* : *trans* ratio. According to quantum chemical modelling of the decamers of metathesis poly(5-trimethylsilylnorbornene), the formation of helical fragments in the chains of this polymer is possible only in the presence of regular repetition of *cis*-configured C=C double bonds.[66] The inclusion of only *trans*-units or alternation of the *cis* and *trans* units results in statistical coil conformation for the decamers and possibly a closer packing of the macrochains.

The introduction of an additional double bond into the polynorbornene five-membered ring and the resulting somewhat different arrangement of substituents (in the same plane as the substituted double bond) (Table 3) do not induce substantial changes in the gas permeability.

The replacement of one or two methyl groups in the trimethylsilyl substituent by Ph, Pr^i or CH_2SiMe_3 reduces the gas permeability coefficients (see Table 3). The introduction of CH_2SiMe_3 groups instead of one methyl group considerably decreases the glass transition temperature due

Table 3. Gas separation characteristics of metathesis polynorbornenes, polynorbornadiene and polytricyclononene with one silicon-containing substituent in the monomer unit.

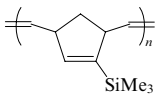
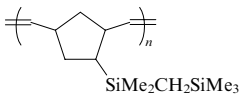
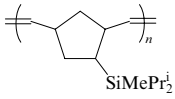
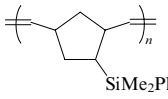
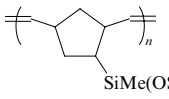
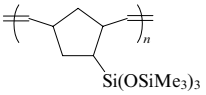
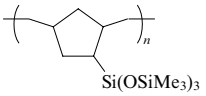
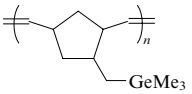
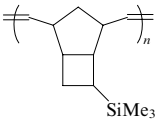
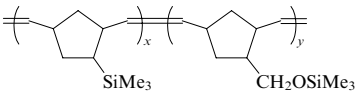
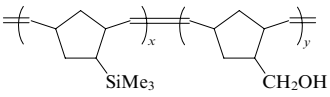
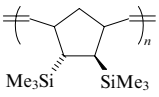
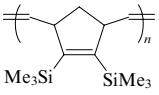
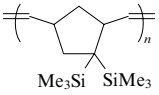
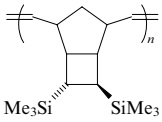
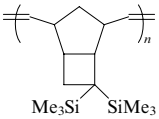
Polymer	T_g /°C	*P* /Barrer					α_{AB}		Ref.
		H_2	N_2	O_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4	
	108 [a]	81.0	4.9	20.0	64.0	8.5	4.1	7.5	38
	24	73.0	3.7	16.0	67	8.5	4.3	7.9	29
	110	58.3	3.9	13.5	51.9	7.3	3.5	7.1	36
	57	16.5	0.45	2.0	9.1	0.8	4.4	11.4	36
	27	230	30	99	430	87	3.3	4.9	35

Table 3 (continued).

Polymer	T_g/°C	P/Barrer					α_{AB}		Ref.
		H_2	N_2	O_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4	
	101	430	93	290	910	260	3.1	3.5	35
	62	320	55	160	610	160	2.9	3.8	35
	48	34.9	1.8	7.7	29.4	4.2	4.3	7.0	37
	104	119	6.8	28	112	14.3	4.1	7.8	36
	73 [b]	39.1	2.4	9.8	43.9	5.9	4.1	7.4	34
	105 [b]	51.4	2.6	9.9	45.4	4.9	3.8	9.3	34

[a] In this case, W-based catalyst was used, and in the other cases, Ru-based systems were used as catalysts; [b] statistical copolymers, $x \approx 0.7$.

Table 4. Gas separation characteristics of polynorbornenes, polynorbornadienes and polytricyclononenes with two silicon-containing substituents in the monomer unit.

Polymer	T_g/°C	P/Barrer					α_{AB}		Ref.
		H_2	N_2	O_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4	
	167 [a]	375	25	95	445	45	3.8	9.9	38
	183	254	20	71	358	48	3.6	7.5	34
	203	218	14	54	277	27	3.9	10.2	34
	129	332	24	89	396	55	3.7	7.2	34
	188	209	12	50	258	28	4.2	9.2	36

[a] In this case, Ru-based catalyst was used and in the other cases, W-based systems were used as catalysts.

to self-plasticization of the polymer, which, in turn, allows a closer packing of the macromolecules. This situation is observed not only for the homopolymer but also for copolymer where the norbornene with the CH_2OSiMe_3 substituent, *i.e.*, with a OCH_2 bridge between the norbornene fragment and the trimethylsilyl group, is used as the comonomer with 5-trimethylsilylnorbornene (see Table 3). The replacement of the CH_2OSiMe_3 group in the copolymer by CH_2OH increases somewhat the glass transition temperature and hydrogen permeability of the copolymer. Apparently, the presence of hydroxy groups leads to the formation of intra- and interchain hydrogen bonds in the copolymer (their presence was detected in the IR spectrum [34]); this gives rise to a more rigid polymer structure. Although both copolymers contain mainly 5-trimethylsilylnorbornene units ($\sim$70%), the effect of the units introduced by the second comonomer on the transport parameters is rather noticeable (the permeability decreases 1.5–2-fold).

A considerable effect was achieved by the introduction of the second $SiMe_3$ group into the monomer unit of poly(5-trimethylsilylnorbornene) (Table 4). This modification induces a 3–4-fold increase in the gas permeability coefficient not only for polynorbornenes but also for structurally analogous polytricyclononenes. The effect of the introduction of the second $SiMe_3$ group is most pronounced if these groups are *trans*-vicinally arranged, while the minimum effect corresponds to the geminal arrangement (see Table 4). This may be due to the somewhat different structure of free volume in the case of geminal substituents. The replacement of the methyl groups in the $SiMe_3$ fragments by $OSiMe_3$ groups considerably increases the permeability.[35] An increase in the degree of replacement of the methyl groups by $OSiMe_3$ is accompanied by increase in both the glass transition temperature and the gas permeability coefficient. Using this approach, poly[5-tris(trimethylsiloxy)silylnorbornene] with fairly high permeability was obtained [35] (see Table 3). Hydrogenation of this polymer reduces the glass transition temperature and gas separation parameters, which is attributable to the higher chain flexibility caused by the presence of two bridging methylene groups between the cyclopentane rings. Flexible macromolecules are packed more closely, thus decreasing the free volume and the polymer permeability.

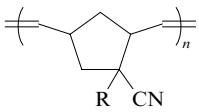
The residual content of the catalyst in the polymer is significant for the gas separation characteristics. As a rule, by a 2–3-fold reprecipitation of metathesis polynorbornenes, this content can be reduced to acceptable values. Thus the residual content of Ru in silicon-substituted polynorbornenes determined by inductively coupled plasma atomic emission spectroscopy was $\leqslant$60 ppm.

2. Cyano-substituted polynorbornenes

Table 5 presents the permeability coefficients for a number of cyano derivatives of polynorbornene with different substituents in the geminal position.[27] It can be seen that this series of polynorbornenes has rather low P values. Apparently, this is related to strong interchain dipole–dipole interactions of the CN groups ensuring close packing of polymer chains.

The introduction of the alkyl substituent into the geminal position to the CN group results in a decrease in the glass transition temperature as a result of the self-plasticizing effect of polymers with alkyl side groups (see Table 5). As the alkyl group is elongated, the permeability increases. Probably, the introduction of geminal alkyl substituents produces some increase in the interchain distances, *i.e.*, decrease in the polar effect of the cyano groups, and, hence, this increases the free volume. The introduction of the trimethylsilyl group into the geminal position causes substantial increase in the glass transition temperature and increase in the permeability (see Table 5). Probably, the bulky $SiMe_3$ group not only increases the interchain distances but also enhances the chain rigidity and, hence, increases the free volume of polynorbornene. The most pronounced effect came from introduction of the $SiMe_2OSiMe_3$ groups; along with the growth of gas permeability of polynorbornene, this induced a decrease in T_g.

Table 5. Gas separation characteristics of various cyano-substituted polynorbornenes obtained using a W catalyst.[27]



R	T_g/°C	P/Barrer		α_{O_2/N_2}
		O_2	N_2	
H	140	0.53	0.084	6.3
Et	134	1.7	0.32	5.2
Pr^n	108	2.0	0.40	5.0
Bu^n	87	2.4	0.52	4.6
$SiMe_3$	211	7.6	1.65	4.6
CH_2SiMe_3	128	11.0	2.62	4.2
$SiMe_2SiMe_3$	120	4.4	0.96	4.6
$SiMe_2OSiMe_3$	88	15.3	3.48	4.4

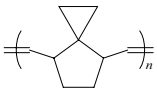
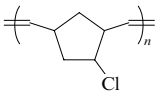
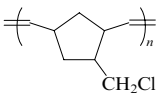
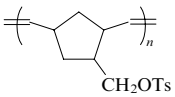
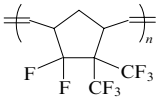
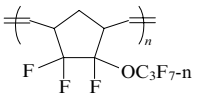
3. Alkyl-, tosyl- and halo-substituted polynorbornenes

Some studies considered the effect of chloro-, fluoro- and alkyl-containing groups on the permeability of metathesis polynorbornenes.[49, 50, 61] The obtained data are presented in Table 6. A decrease in the gas permeability values after the introduction of a cyclopropyl group into polynorbornene was interpreted [49] as being due to filling of the free volume in the polymer by cyclopropyl groups.

The introduction of chlorine substituents reduced the gas permeability coefficients for all of the studied gases (see Table 6). The most pronounced decrease with respect to the value for unsubstituted polynorbornene occurs for the chloromethyl substituent. The decrease in the permeability in the presence of chlorine atoms as side groups was attributed to interchain dipole–dipole interactions, which promote a close packing of the macromolecules. The replacement of chlorine in the chloromethyl fragment by a tosylate group reduces the gas permeability, probably, due to the appearance of the flexible C–O–C fragment.

Good gas separation characteristics were found for fluorine-containing polynorbornenes (see Table 6).[50] The presence of two polar CF_3 groups in a monomer unit causes a considerable increase in the glass transition temperature (169 °C) and increase in the permeability coefficients as compared with unsubstituted polynorbornene (T_g = 37 °C). The introduction of bulky and polar CF_3 groups is likely to decrease the chain mobility, thus preventing the close packing of macromolecules and maintaining a large free volume. Yet another possible cause of the higher gas permeability [50] is the increase in the solubility coefficients of gases in fluoro-substituted polynorbornenes. The

Table 6. Gas separation characteristics of halogen-containing and some hydrocarbon derivatives of polynorbornenes.

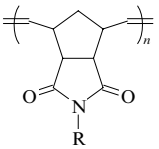
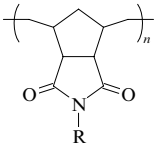
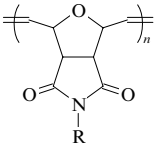
Polymer	T_g/°C	P/Barrer						α_{AB}		Ref.
		H_2	N_2	O_2	CO_2	CH_4	C_2H_6	O_2/N_2	CO_2/CH_4	
	50	7.0	0.3	1.0	2.0	0.4	0.2	3.3	5.0	49
	–	17.5	0.89	2.3	8.3	1.3	–	2.6	6.4	49
	–	3.0	0.24	0.46	–	0.23	0.057	1.9	–	49
	95	–	0.06	0.39	–	–	–	6.5	–	61
	169	166	17	50	200	13	6.6	2.9	15.4	50
	77	130	17	55	200	18	14	3.2	11.1	50

replacement of one CF_3 group in the polymer by OC_3F_7-n decreases T_g to 77 °C, while the permeability coefficients change little (see Table 6). Note that fluoro-substituted polynorbornenes have an important feature: they are insoluble in hydrocarbons, which is attractive as regards their practical use.

4. Polymeric norbornenedicarboximide derivatives

Polynorbornenes containing an imide group are being studied in detail by a team of Mexican scientists [51–58] as a possible alternative to polyimides — industrial polymers with low permeability but high gas separation selectivity.[67] Table 7 summarizes the data obtained for various imide

Table 7. Gas separation characteristics of metathesis dicarboximide polynorbornene and polyoxanorbornene derivatives.

Polymer	R	T_g /°C	P/Barrer					α_{AB}			Ref.
			H_2	N_2	O_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4	H_2/N_2	
	cyclo-C_5H_9	174	–	0.45	1.95	8.8	0.54	4.3	16.3	–	55
	cyclo-C_6H_{11}	155	–	0.43	2.3	9.2	0.48	5.3	19.2	–	55
	cyclo-C_6H_{11} (see [a])	129	16.1	0.61	2.13	18.11	1.12	3.5	16.2	26.4	54
	Ad	271	12.8	0.50	1.59	8.39	0.58	3.2	14.5	25.6	54
	Ph	222 [b]	11.0	0.31	1.44	11.44	0.54	4.6	21.2	35.5	53, 54
	C_6F_5	171	38.50	1.55	6.08	25.17	1.37	3.9	18.4	24.8	58
	4-$CF_3C_6H_4$	155	–	3.69	15.5	77.5	4.09	4.2	18.9	–	51
	3,5-$(CF_3)_2C_6H_3$	168	57.41	4.20	13.53	67.26	4.28	3.2	15.7	13.7	58
	Ph	197	7.22	0.12	0.66	4.51	0.15	5.5	30.1	60.2	53, 56
	$HSO_3C_6H_4$	> T_d	4.25	0.0043	0.27	1.98	0.0048	62.8	412.5	988	53
	C_6F_5	187	22.92	1.08	3.55	16.30	1.13	3.3	14.4	21.1	58
	3,5-$(CF_3)_2C_6H_3$	182	–	11.3	39.4	164.6	10.7	3.5	15.4	–	51, 57

[a] The polymer obtained from 100% *exo*-isomer; [b] according to Ref. 53, 233 °C according to Ref. 54.

derivatives of polynorbornene and poly(7-oxanorbornene). By introduction of bulky cyclic substituents (cyclo-C_5H_9, cyclo-C_6H_{11}, Ad) to nitrogen, it was possible to increase the rigidity of the backbone, and the glass transition temperature of the polymers increased to 155–271 °C. Nevertheless, the gas permeability of polynorbornenes remained rather low, probably, due to strong interchain interaction of polar dicarboximide groups. The introduction of a phenyl group entailed a decrease in the permeability coefficients, which can be attributed to the ability of the benzene rings to form close packing.

Hydrogenation of the polymer, for example, poly(*N*-phenyl-*exo*,*endo*-norbornene-5,6-dicarboximide), decreases both the glass transition temperature and the permeability coefficients of the polymer. The same effect is observed upon hydrogenation of silicon-substituted polynorbornenes (see above). The appearance of two bridging methylene groups between the cyclopentane rings instead of the double bond enhances the chain flexibility and favours closer packing of macromolecules. Sulfonylation of the reduced poly(*N*-phenyl-*exo*,*endo*-norbornene-5,6-dicarboximide) increases the glass transition temperature ($T_g > T_d$, T_d is the decomposition temperature) and decreases the permeability. In all of the cited examples, the gas permeability coefficients are inversely related to the selectivity of gas separation.

The introduction of fluorine-containing substituents to the N atom of the norbornenimide fragment induces the most pronounced increase in the permeability of polymers at relatively high separation factors. This effect is especially pronounced when a CF_3 group is introduced in the benzene ring.

In a study of gas separation characteristics of various norbornene copolymers with N-substituted norbornene-5,6-dicarboximide and 7-oxanorbornene-5,6-dicarboximide, a dependence of permeability coefficients on the copolymer composition typical of copolymers was observed. However, no correlation was found between the copolymer composition and the gas separation selectivity (Table 8).[52, 54]

It was shown[51–58] that the permeability of most polymers based on N-substituted norbornene-5,6-dicarboximides is mainly controlled by diffusion rather than by the solubility of gases.

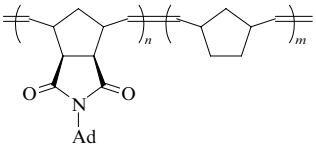
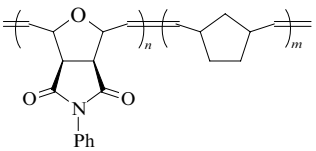
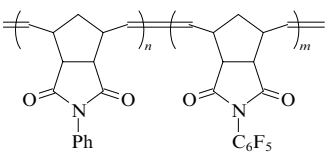
For a number of polynorbornenes that were used as materials for optical oxygen sensors, the oxygen permeability was studied.[62] The monomer units of these polynorbornenes contained two substituents with ester or keto groups having various bulky groups attached to them (see monomers **5a**–**h**). The data obtained do not allow one to compare the gas permeabilities of the polymers studied with other polynorbornenes, as the estimation was performed in other units by a procedure used for evaluating the efficiency of sensors. Only the trends can be considered, in particular, higher permeabilities were found for polynorbornenes with substituents in which the bulky group was attached directly to the oxygen-containing fragment without an aliphatic spacer. The polymer obtained from monomer **5g** showed the best properties.

IV. Addition polymerization of norbornenes as a method for the synthesis of membrane materials

As noted above, metathesis polynorbornenes are convenient objects for the systematic investigation of the gas separation characteristics. Some $SiMe_3$ derivatives of polynorbornene demonstrated high permeability and selectivity with respect to light gases (see Tables 3, 4). For these compounds, it was shown unambiguously that an increase in the number of $SiMe_3$ groups in a monomer unit from 0 to 3 leads to systematic increase in the permeability. However, all metathesis polymers have a common drawback, namely, low thermal and chemical stability due to the presence of double bonds. However, upon hydrogenation of unsaturated polynorbornenes, the permeability considerably decreases[35] due to the decrease in the rigidity of the polymer chain.

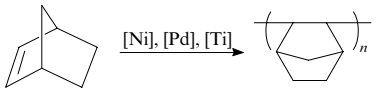
The stability problem of polynorbornenes can be in principle solved by implementing an alternative (addition) polymerization of norbornenes, which results in completely

Table 8. Gas separation characteristics of metathesis copolymers of norbornene with dicarboximide derivatives of norbornene and 7-oxanorbornene.

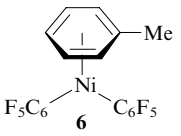
Polymer	$n:m$	T_g /°C	P/Barrer					α_{AB}			Ref.
			H_2	N_2	O_2	CO_2	CH_4	H_2/N_2	O_2/N_2	H_2/CH_4	
	7:3	202	18.5	0.60	1.92	8.13	0.96	30.8	3.2	19.3	54
	1:1	117	10.7	0.22	1.21	5.11	0.42	48.6	5.5	25.5	54
	3:7	80	12.2	0.43	1.40	–	0.60	28.4	3.2	20.3	54
	1:1	125	9.21	0.21	0.99	6.14	0.27	43.8	4.7	34.1	52
	1:1	205	19.55	0.59	2.66	16.51	0.64	33.1	4.5	30.5	58

saturated rigid macromolecular structures. The addition polymerization (AP) is energetically less favourable process than ROMP.[1] There is no so high thermodynamic driving force; therefore, the range of active substrates and catalysts is much narrower than in the case of ROMP.

Unsubstituted norbornene is one of the most AP-active cycloolefins. The addition polymerization of norbornene has been studied in the presence of a large number of catalytic systems containing Ni, Co, Pd, Ti, Cr and Fe.[19]



Most often, transition metal salts are used as the catalysts and boron and aluminium compounds are used as activators, although there are some nickel and palladium complexes (for example, compounds **6**, **7**) that are known to perform the AP of norbornene without an activator.



6

$[Pd(RCN)_4]^{2+}[BF_4]^-_2$

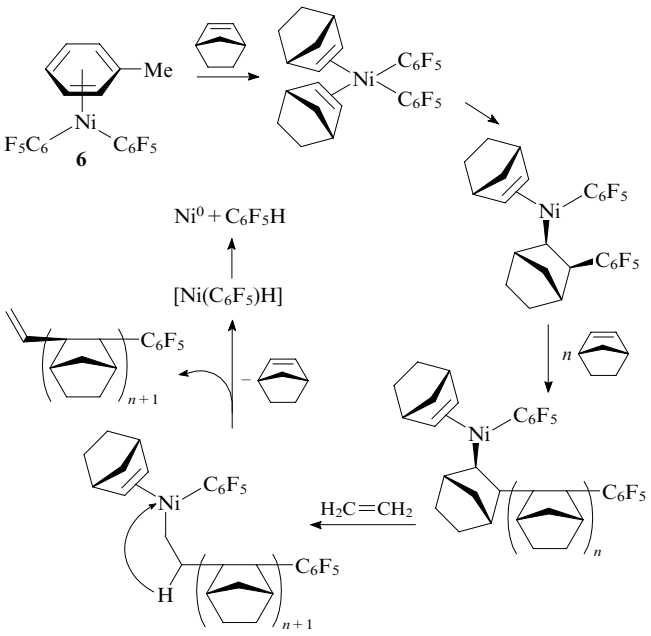
7

R = Me, Et.

It is believed [19, 68, 69] that these catalysts should contain one or two very labile ligands (for example, PhMe or RCN) and a pentafluorophenyl group.

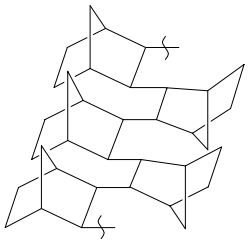
A polymerization mechanism was proposed for nickel complex **6** (Scheme 3).[68] The mechanism was established using ethylene-induced chain termination. According to ^1H and ^{19}F NMR spectroscopy, the $CH{=}CH_2$ and C_6F_5 terminal groups were found. The process starts with insertion of norbornene by the *exo*-side into the $Ni-C_6F_5$ bond, and this is followed by chain propagation. After insertion of ethylene, the possibility for hydrogen β-elimination appears, and thus the chain is terminated.[68]

Scheme 3



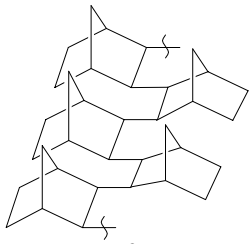
Among the complexes that perform the AP of norbornene, nickel and palladium compounds were most active, the highest activity being revealed [19] for nickel complexes ($> 10^9$ g of polymer per mole of the metal per hour).

The addition polynorbornene is characterized by high thermal (up to 450 °C) and chemical stability and transparency.[70] However, the samples of this polymer obtained using different catalytic systems had different physicochemical properties, in particular, unequal permeability coefficients. This can be attributed to different microstructures of polynorbornenes (for example, structures **8**, **9**) formed in the presence of different catalysts.[19, 71]



8

2,3-*erythro*-Diisotactic

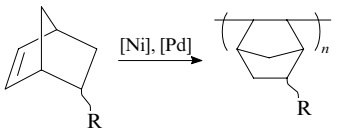


9

2,3-*erythro*-Disyndiotactic

1. Polynorbornenes with alkyl substituents

It was shown using numerous examples that the introduction of any substituent into the norbornene molecule decreased the monomer reactivity towards the AP.[19] The polymerization of 5-alkylnorbornenes in the presence of various Ni and Pd systems and the properties of the polymers obtained in these reactions were studied.[71–74]

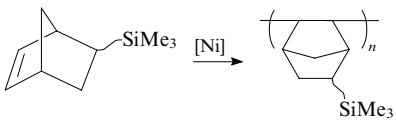


R	T_g /°C	R	T_g/°C
H	≫ 270	n-C_6H_{13}	280
Me	> 380	n-$C_{10}H_{21}$	150
Bu^n	> 350		

Slight differences were detected between the densities and free volumes of the polymers obtained using Ni and Pd catalysts, and substantial differences (2–3-fold) were found between the gas permeability coefficients (see Section V).[71, 74]

2. Silicon-substituted addition polynorbornenes

5-Trimethylsilylnorbornene, a monomer with a bulky side substituent, was successfully involved into AP (Table 9).[75, 76] Note that this monomer exhibited high activity only in the presence of Ni-based catalysts containing organoaluminium compounds, while Pd-based catalysts had very low activity. The homopolymer did not show glass transition temperature up to decomposition.



As noted above (see Section II.1), the synthesis of this monomer performed by the Diels–Alder reaction affords an equimolar *exo*/*endo*-isomer mixture. During the AP, the *exo*-isomer was consumed much faster than the *endo*-iso-

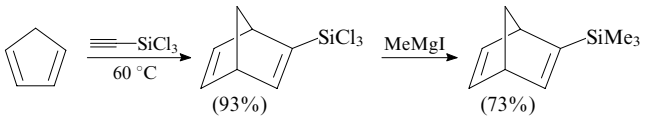
Table 9. Addition polymerization of 5-trimethylsilylnorbornene on nickel catalysts.[75, 76]

Catalyst [a]	The [M] : [Cat] ratio	Time /h	Yield (%)	Conversion of isomers (%)		$M_w \times 10^{-3}$	M_w/M_n
				exo	*endo*		
$(\pi\text{-PentNiCl})_2 - Et_3Al_2Cl_3$ (Al : Ni = 3)	600	48	56	83	28	41	1.7
$(\pi\text{-PentNiCl})_2 - MAO$ [a] (MAO : Ni = 100)	600	96	80	98	61	104	1.8
$Nph_2Ni - MAO$ (MAO : Ni = 100)	1000	24	56	69	27	260	2.0
$(PPh_3)_4Ni - Et_2O \cdot BF_3$ (B : Ni = 300)	600	27	12	–	–	20	1.7

[a] Pent is pentenyl (C_5H_9), MAO is methylalumoxane, Nph is naphthenate.

mer; in other words, the latter showed much lower activity.[76]

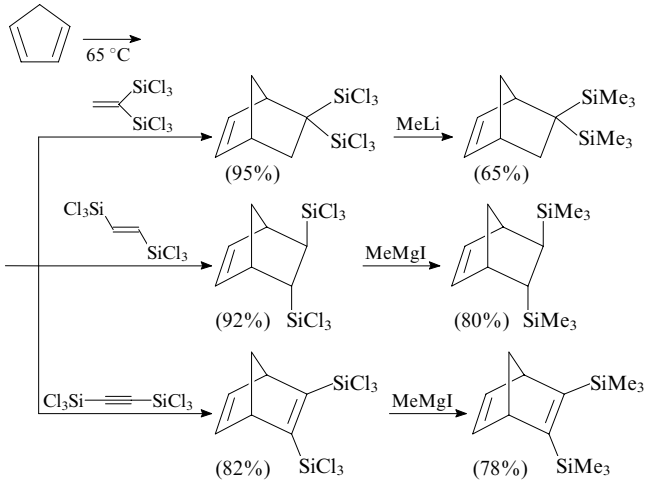
It is noteworthy that a close analogue of 5-trimethylsilylnorbornene, 5-trimethylsilylnorbornadiene, is absolutely inactive in the AP on either nickel or palladium systems; in the authors' opinion,[77] this may be related to stronger coordination of this monomer to the catalyst active site.



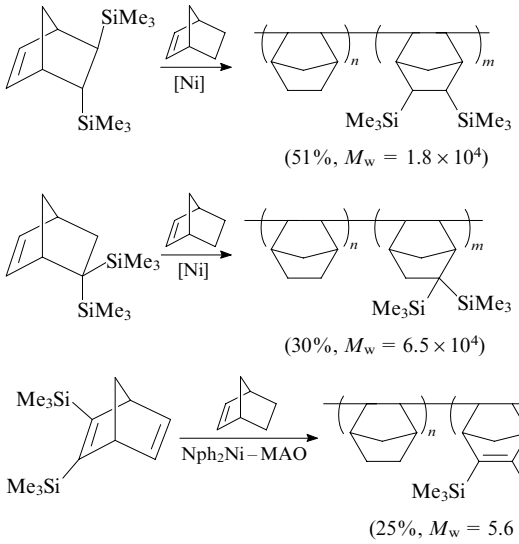
Owing to the presence of the $SiMe_3$ substituent, the addition poly(5-trimethylsilylnorbornene) showed high gas permeability, which was an order of magnitude (or more) greater than the permeability of the unsubstituted polynorbornene.[75]

It was shown [35, 38] that the introduction of two or three $SiMe_3$ groups into the monomer unit of metathesis polynorbornene entails a considerable increase in the permeability with retention of the selectivity level. Therefore, attempts were made [44, 76] to prepare addition polynorbornene with two $SiMe_3$ groups in the monomer unit. To this end, norbornenes were obtained in which the $SiMe_3$ groups occupied different positions, thus creating different steric pressures on the unsubstituted double bond (Scheme 4).[38, 39, 44]

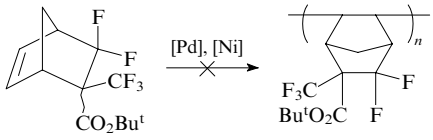
Scheme 4



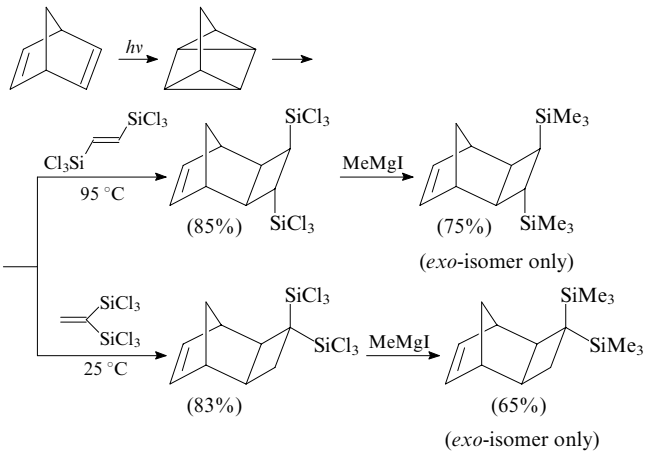
All of the monomers shown in Scheme 4 did not undergo AP in the presence of either nickel- or palladium-based catalysts. This behaviour might be caused by the steric restrictions created by the bulky $SiMe_3$ groups that hamper initiation and chain propagation processes in the active site. However, all of these monomers were copolymerized with norbornene to give the corresponding copolymers in moderate yields (20% – 40%) and with moderate molecular masses [$(3-8) \times 10^4$]. The degree of incorporation of the silicon-containing monomer depended on the composition of the starting mixture and varied in the range of 15% – 35%.[44, 76]



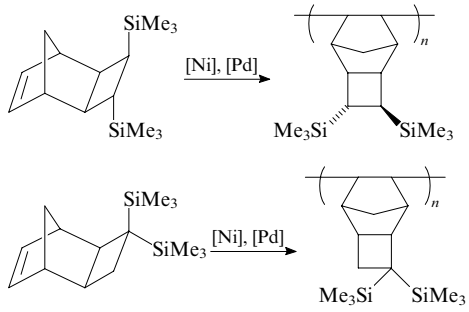
Grubbs and co-workers [78] have faced a similar problem, *i.e.*, the lack of reactivity of polysubstituted norbornenes, in particular, fluorinated ones, towards AP. The lack of reactivity of fluoronorbornenes is apparently related to electronic factors, which the authors managed to mitigate by moving the electron-withdrawing groups (F, CF_3) away from the double bond by one C – C bond.



For this reason, Gringolts *et al.*[79] undertook the synthesis of the norbornene type monomer in which the bulky $SiMe_3$ groups were removed away from the active double bond and no *endo*-substituents were present. The importance of the second requirement is due to the fact that *endo*-derivatives of norbornene are substantially less reactive than the *exo*-isomers.[69, 80] Such monomers, namely, *exo*-tricyclononenes, were synthesized using [2 + 2 + 2]-cycloaddition of quadricyclane to the corresponding olefins.



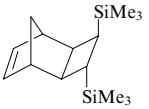
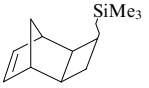
Disubstituted silicon-containing tricyclononene exhibited high reactivity towards AP on both nickel and palladium systems.[44, 79]

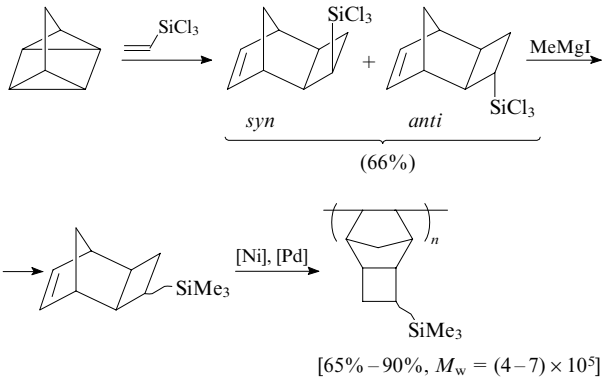


Homopolymers of silicon-substituted tricyclononenes with molecular masses of up to 7×10^5 were prepared in up to 98% yields using the $Pd(OAc)_2 - B(C_6F_5)_3$ catalytic system proposed for the first time for addition polymerization (Table 10). The resulting polymers demonstrated high thermal stability (up to 340 °C) and no glass transition temperature before the onset of decomposition;[44, 79] the residual contents of palladium and boron in the polymer were 70 and 50 ppm, respectively.

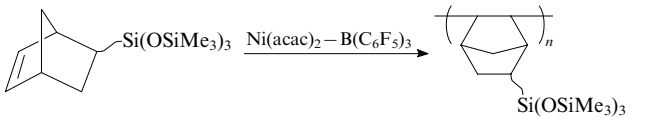
An analogue of addition poly(5-trimethylsilylnorbornene), *viz.*, addition poly(3-trimethylsilyltricyclonon-7-ene), was synthesized and the gas separation characteristics of the polymers were compared.[36, 79] Poly(3-trimethylsilyltricyclonon-7-ene) with desired film-forming properties was successfully obtained on both nickel- and palladium-based catalysts, which made it possible to evaluate the effect of the type of catalytic system on the gas permeability (see Section V).

Table 10. Addition polymerization of mono- and bis(trimethylsilyl)-tricyclononenes in the presence of $Pd(OAc)_2 - B(C_6F_5)_3$.[79]

Monomer (M)	The M : Pd : molar ratio	Polymer yield (%)	$M_w \times 10^{-3}$	M_w/M_n
	1500 : 1 : 75	98	420	2.8
	3200 : 1 : 15	25	394	2.0
	3200 : 1 : 150	60	673	1.7
	6000 : 1 : 200	37	730	1.5
	4000 : 1 : 200	72	574	2.5
	6000 : 1 : 200	35	700	1.7

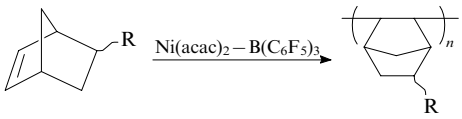


As noted in Sections II.1, Japanese authors[35, 81] increased the number of $SiMe_3$ groups in polynorbornene units to three in order to enhance gas separation characteristics. They performed the AP of the corresponding monomer to give a polymer with three $OSiMe_3$ substituents in the side group; however, this polymer did not have high molecular mass or film-forming properties suitable for permeability measurements.



acac is acetylacetonate.

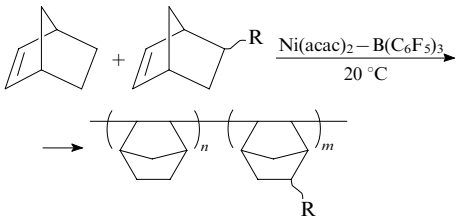
Apart from 5-tris(trimethylsiloxy)silylnorbornene, the researchers cited[81] investigated the AP behaviour of two other potentially interesting silicon-containing monomers.



R = cyclo-$SiMeO(SiMe_2O)_3$ (12%, $M_n = 2.7 \times 10^4$),
$SiMePhOSiMe_3$ (45%, $M_n = 4.2 \times 10^4$).

However, these homopolymers also had low molecular masses and were formed in moderate yields.

A way of solving the problem of enhancing the mechanical strength and film-forming properties of the polymers is the synthesis of copolymers in which the second component is responsible for good mechanical characteristics. Norbornene copolymers with 5-oligosiloxanylnorbornene of various compositions were obtained for this purpose.[81]

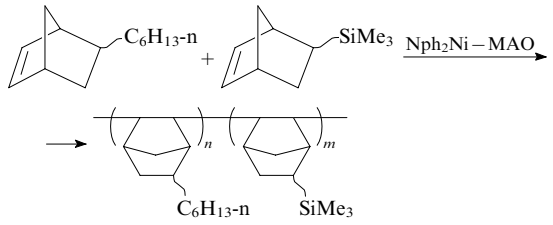


R	Yield (%)	T_g/°C	$M_n \times 10^{-5}$
$Si(OSiMe_3)_3$	65	343	1.98
cyclo-$SiMeO(SiMe_2O)_3$	26	293	1.4
$SiMePhOSiMe_3$	43	327	1.61

Unlike the corresponding addition homopolymers, the copolymers had admissible film-forming properties (elongation at rupture of up to 14%, ultimate tensile strength of 31–71 MPa). Their molecular masses were higher than those of 5-oligosiloxanylnorbornene homopolymers, and the glass transition temperatures were lower than the decomposition temperatures. If the content of the siloxane monomer exceeded 20 mol.%, the copolymers were soluble in hexane and decane but insoluble in dichloromethane. The highest yields were reached for 5-tris(trimethylsiloxy)silylnorbornene, which attests to a certain influence of the substituent on the copolymerization, although the composition of the copolymer did not depend on the substituent nature.

The lack of cross-linking or Si–O–Si bond rupture during homopolymerization was proved by ^{29}Si NMR spectroscopy.

In order to enhance the film-forming properties of addition poly(5-trimethylsilylnorbornene), its copolymer with 5-hexylnorbornene was synthesized.[75]



(63%, $M_w = 4.42 \times 10^5$)

V. Gas separation properties of addition polynorbornenes

As regards the gas permeability coefficients, this group of polymers appreciably surpasses the metathesis analogues. Table 11 summarizes the results of measurement of gas separation characteristics for various addition poly(5-alkylnorbornenes) and polynorbornene.

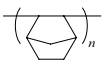
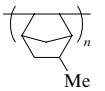
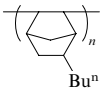
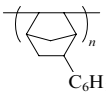
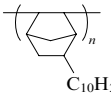
It can be seen that the permeability characteristics of the same polymer depend considerably on the nature of the polymerization catalyst. For example, the use of different salts of the same metal results in permeability change by ~50% in the case of unsubstituted polynorbornene.[75,82] Even more pronounced is the effect observed for addition poly(5-methylnorbornene) for which these parameters differ by a factor of two or more depending on the salt used.[71] Wilks *et al.*[71] attributed this effect to different microstructure of the polymers formed on different catalysts. In particular, they assigned only 2,3-*erythro*-diisotactic structure of unit coupling (**8**) to addition poly(5-methylnorbornene) obtained using a Pd-based catalytic system, whereas in the presence of Ni-based catalyst, they assumed the formation of a mixed structure [25% of 2,3-*erythro*-disyndiotactic (**9**) and 75% of 2,3-*erythro*-diisotactic structure (**8**)].

The introduction of an alkyl substituent into the norbornene molecule decreases the glass transition temperatures of addition poly(5-alkylnorbornenes) following the elongation of the side chain, which is attributable to self-plasticizing effect. Decomposition temperature also decreases. The data of Table 11 indicate that the gas separation characteristics of addition poly(5-alkylnorbornenes) are at a moderate level.

Zhao *et al.*[82] investigated the permeability of unsubstituted addition polynorbornene samples with various molecular masses for three gases (O_2, CO_2, N_2) at different pressures (1, 2.5, 4 atm). The authors did not find any significant influence of the molecular mass on the permeability.

Irrespective of the type of polymerization catalyst, the introduction of a methyl group into the norbornene unit

Table 11. Gas separation characteristics of addition poly(5-alkylnorbornenes) and polynorbornene.

Polymer	Catalyst	T_g/°C	P/Barrer					α_{O_2/N_2}	Ref.
			H_2	N_2	O_2	CO_2	CH_4		
	[Ni]	>350	41.5	1.5	6.9	33.6	2.6	4.5	75
	[Ni]	>300	–	2.7	10.8	49.1	–	4.0	82
	[Pd]	>300	–	12.6	–	202.1	16.9	–	71
	[Ni]	>300	–	4.3	–	81.1	5.6	–	71
Me	see [a]	>380	502.1	24.1	89.2	396.3	30.3	3.7	74
	see [a]	>350	110.7	11.2	33.3	141.9	28.4	3.0	74
Bu^n									
	see [a]	280	57.2	6.9	19.8	83.8	18.7	2.9	74
C_6H_{13}-n									
	see [a]	150	62.4	8.7	25.3	111.1	28.1	2.9	74
$C_{10}H_{21}$-n									

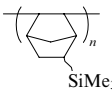
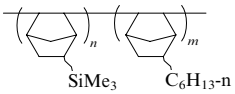
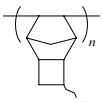
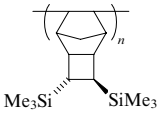
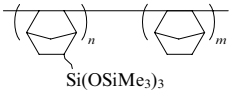
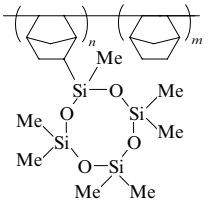
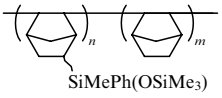
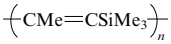
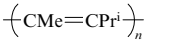
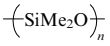
[a] In this work, polymer pre-synthesized with organometallic catalysts were used.

induces an increase in the permeability of all gases. The presence of a longer-chain alkyl substituent causes a decrease in the permeability parameters compared with addition poly(5-methylnorbornene).[74] This may be due to the plasticization effect induced by the flexible side substituent. However, it was noted that the permeability parameters no longer decrease on going from the hexyl to decyl group.

The most pronounced growth of gas permeability coefficients in the case of addition polynorbornenes was induced by introduction of the $SiMe_3$ side groups; the gas permeability parameters increased by 1.5 orders of magnitude as compared with unsubstituted polynorbornene (Table 12). This sharp increase was interpreted [75] as being caused by the considerable increase in the free volume upon the introduction of the bulky side substituent. Note that as regards the permeability level, the synthesized addition copolymer of 5-trimethylsilylnorbornene with 5-n-hexylnorbornene occupies an intermediate position between the corresponding homopolymers.

The silicon-substituted polytricyclononenes described recently are no less interesting for membrane gas separation. Monosubstituted addition poly(3-trimethylsilyltricyclonon-7-ene) was successfully synthesized on two catalytic systems, nickel- and palladium-based ones.[36, 79] The permeability of the polymer obtained on the palladium catalyst is much higher, which is consistent with the properties of addition poly(5-methylnorbornenes), and can be caused by different microstructures of the polymers formed in the presence of different catalytic systems. It is noteworthy that the permeability coefficients of addition poly(3-trimethylsilyltricyclonon-7-ene) obtained using ternary Ni-based catalyst are below the permeability parameters of addition poly(5-trimethylsilylnorbornene) prepared in the presence of binary Ni-based catalyst,[75] and the permeability of addition poly(3-trimethylsilyltricyclonon-7-ene) obtained

Table 12. Permeability of addition silicon-substituted polynorbornenes and some highly permeable polyacetylenes and polysiloxanes.

Polymer	Catalyst	T_g/°C	P/Barrer					Ref.
			H_2	N_2	O_2	CO_2	CH_4	
	[Ni]	> 300	1680	297	780	4350	800	75
 $n : m = 64 : 36$	[Ni]	> 300	164	19	60	330	48	75
	[Pd]	> 300	2100	400	1000	5300	1000	79
	[Ni]	142	1200	150	450	2200	400	36
	[Pd]	> 300	4100	1200	2400	11 300	3300	79
 $n : m = 26 : 74$	[Ni]	304	–	–	239	–	–	81
 $n : m = 14 : 86$	[Ni]	293	–	–	28	–	–	81
 $n : m = 23 : 77$	[Ni]	265	–	–	22	–	–	81
		> 250	16700	6300	9700	34 200	15 400	83
		> 250	5800	1330	2700	10 700	2900	84
		−123	–	466	933	4550	1350	85

using Pd-based catalytic system is higher than the corresponding values for the addition poly(5-trimethylsilylnorbornene).

The introduction of the second $SiMe_3$ group into the monomer unit of addition poly(3-trimethylsilyltricyclonon-7-ene) induces further (2–3-fold) increase in the gas permeability coefficients.[79] As regards this value, polytricyclononene with two $SiMe_3$ side groups in every monomer unit proved to be at the same level as the most permeable polymers, *i.e.*, polyacetylenes.

Apart from homopolymers, Table 12 presents data for copolymers. In particular, it was shown[81] that an increase in the content of norbornene units in these addition copolymers deteriorates the permeability characteristics.

It can be seen from the data given in Table 12 on the addition copolymers of silicon-substituted norbornenes with norbornene that only the introduction of a trimethylsilyl group increases the permeability. The replacement of the substituent at silicon by the phenyl group or the oligosiloxane fragment sharply deteriorates the membrane properties.

Interesting results were obtained in the study of lower n-alkane permeability of silicon-substituted polynorbornenes.[75, 79, 86] It was found that in the series of n-alkanes, the permeability coefficients are higher for larger penetrant molecules (Table 13), *i.e.*, in this case, the permeability is rather determined by sorption thermodynamics than by diffusion. This type of behaviour is typical of rubbers and not of glassy polymers. Before the publication of works on the synthesis and study of properties of silicon-substituted addition polynorbornenes, this type of behaviour was observed only for some highly permeable polyacetylenes.[12]

It can be seen from the results given in Table 13 that the gas permeability parameters of silicon-substituted polynorbornenes with respect to hydrocarbon gases are comparable to those of the most permeable polymers: 1,2-disubstituted polyacetylenes. The selectivity with respect to the n-C_4H_{10}/CH_4 pair is equal to or higher than this parameter for polyacetylenes.

Data on ageing of silicon-substituted addition polynorbornenes indicating their high stability were reported.[75, 79] The oxygen and nitrogen permeabilities of these polymers almost did not change after 20-day storage at 20–80 °C.

The addition silicon-substituted polynorbornenes considered above show not only high gas separation characteristics and thermal and chemical stabilities but also the required film-forming properties and, hence, they can be considered as promising membrane materials for the separation of natural C_1-C_4 hydrocarbon gas mixtures. Their good prospects are supported by the facile methods of synthesis caused by the specific features of the organosilicon chemistry.[87]

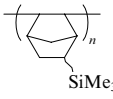
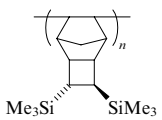
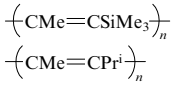
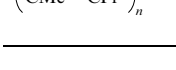
VI. Conclusion

Analysis of the published data presented in this review indicates that norbornenes are exceptionally convenient starting compounds for the macromolecular design of membrane materials. This is due to the accessibility of a variety of norbornenes, including ones with bulky substituents, and the unique possibility of obtaining their polymers with controlled rigidity of the backbone and a broad range of side groups.

The efforts of groups of researchers in the USA, Japan, Mexico, Russia and other countries resulted in the development of methods for the synthesis and polymerization of numerous norbornene monomers aimed at the preparation of extensive series of the corresponding polymers needed for elucidating the dependence of gas separation characteristics on the chemical structure of the matrix. The understanding of this dependence made it possible to create macromolecular structures with high permeability and selectivity for light gases (H_2, He, N_2, O_2, CO_2) and C_1-C_4 lower hydrocarbons. These structures include, first of all, addition polynorbornenes with trimethylsilyl side groups.

The synthesis of various (metathesis and addition) polymers of norbornene and its derivatives provides a lot of information for the science of membranes and, in particular, for membrane materials science. The large number of studied metathesis polynorbornene structures provided more specific knowledge on the structure–gas separation properties relationships. In the database 'Gas separation parameters of glassy polymers' founded and maintained at the Institute of Petrochemical Synthesis, Russian Academy of Sciences,[88] the number of metathesis polynorbornenes falls behind only polyimides and polyacetylenes. Using the obtained transport parameters of these polymers, now it is possible to make not only qualitative estimates but also quantitative predictions (using group contribution method) of the permeability and diffusion

Table 13. Permeability coefficients and selectivity of separation of hydrocarbon gases for silicon-substituted addition polynorbornenes and some highly permeable glassy polymers.

Polymer	Catalyst	*P*/Barrer				$\alpha_{n\text{-}C_4H_{10}/CH_4}$	Ref.
		CH_4	C_2H_6	C_3H_8	n-C_4H_{10}		
	[Ni]	800	1400	1700	17500	22.0	75
	[Pd]	1000	1400	1500	13000	13.0	79
	[Pd]	3300	6000	7500	26900	8.2	79
		15400	26000	30300	78800	5.1	83
		2900	3700	7300	40300	13.9	84

coefficients and the corresponding activation energies for a broad range of gases. The results of studies of the structures of addition polymers of norbornene allow one to conclude that silicon-substituted polymers of this class are among the most interesting membrane materials synthesized in recent years. It is especially significant that these materials might provide a solution to one of the key problems of membrane technology, namely, separation of natural and associated gas hydrocarbons according to their molecular masses.

In our opinion, further enhancement of gas separation and mechanical characteristics of polynorbornenes could be attained by combining the level of rigidity of the backbone and the number of bulky side groups.

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